Requested Patent: GB942363A

Title: POLYPROPYLENE RUBBER BLENDS ;

Abstracted Patent: GB942363 ;

Publication Date: 1963-11-20 ;

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Application Number: GB19620004922 19620208 ;

Priority Number(s): US19610089902 19610217 ;

IPC Classification: ;

Equivalents: DE1216539, FR1317450, NL274843

ABSTRACT:

A composition contains a major proportion of isotactic polypropylene in intimate admixture with at least one per cent by weight of each of at least two rubbery materials. Specified rubbery materials are butyl rubber, butadiene rubber (e.g. cis-1,4-polybutadiene), copolymers of butadiene with styrene or acrylonitrile, polyisoprene, polyisobutylene, natural rubber, silicone rubber, polysulphide rubber, and chlorinated and hydrochlorinated rubbers. The compositions find application as boxes, tanks,luggage, automobile and refrigerator parts and as battery boxes.

PATENT SPECIFICATION

942,363

NO DRAWINGS

942,363

Date of Application and filing Complete Specification: Feb. 8, 1962.

No. 4922/62.

Application made in United States of America (No. 89902) on Feb. 17, 1961.

Complete Specification Published: Nov. 20, 1963.

Index at acceptance:—Classes C3, P(2A, 2C13C, 2D1A, 2D1B, 2FX, 2K7, 2K8, 7A, 7C11, 7C13A, 7C13B, 7C13C, 7D1B, 7D1X, 7D2A1, 7K2); C3, Q5X.

International Classification:—C 08 d, f (C 08 c).

COMPLETE SPECIFICATION

Polypropylene Rubber Blends

We, THE DOW CHEMICAL COMPANY, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is performed, to be particularly described in an by the following statement:—

This invention relates to new compositions of matter. More particularly, this invention relates to certain blends comprising polypropylene and rubbery, elastomeric materials.

Polypropylene is a material which is highly regarded by the plastics industry for the reason that it possesses a number of desirable qualities, such as relatively low density, good flexibility, excellent heat resistance and chemical inertness toward both aqueous and non-aqueous liquids. However, polypropylene has been found to be unduly susceptible to fracture by mechanical shock, especially at low temperatures. This defficiency has retarded the use of polypropylene in article which may be struck a sharp blow at temperatures below freezing (0°C.), such as large boxes and tanks, luggage, automobile and refrigerator parts, battery boxes and so forth.

The present invention provides polypropylene compositions of improved impact strength, especially at low temperatures. It further provides polypropylene compositions which are economical to prepare and which can be fabricated into boxes, luggage, tanks and the like, which will have satisfactory resistance to fracture from mechanical shock.

According to the present invention there is provided a composition consisting of or containing a major proportion of isotactic polypropylene in intimate admixture with at least one per cent by weight of each of at least two rubbery materials as specified herein. The addition and intimate blending of one rubber with polypropylene, while it frequently produces an increase in the impact strength of the polypropylene is often accompanied by certain difficulties. These difficulties include the formation of gels in the blend and the production of an undue amount of tackiness. Films extruded from blends of polypropylene and a single rubber have been found to have rough, textured surfaces. The use of two rubbery materials in accordance with the present invention substantially avoids these difficulties and also make it possible to incorporate a greater total quantity of rubber in the polypropylene when desired, than would be possible when only one rubber is employed in the blending. Further, the use of two rubbers facilitates obtaining a more intimate dispersion of the rubber throughout the polypropylene.

Polypropylene suitable for use in the compositions of this invention is a normally solid plastic material having molecular weights ranging from 5,000 to 500,000, especially about 100,00 to about 300,000. The usual commercially available grades which are substantially isotactic and suitable for molding, extrusion, calendering and the like shaping processes can be used.

By the terms "rubber," "rubbery material" and "elastomer" and "derivatives thereof" which are incorporated with polypropylene in the practice of the invention are meant polymeric materials having molecular weights in excess of 1000 and may be of natural or synthetic origin. The preferred polymers are linear in structure and may be saturated or unsaturated. These materials are characterized by being elastic and stretchable and by showing rapid retraction after release of the stretching force. Among the kinds of rubbery materials that can be used to form the composition of this invention are polyisobutylene, butyl rubber, butadiene rubber, rubbery copolymers of butadiene and styrene, rubbery copo-

lymers of butadiene and acrylonitrile, isoprene rubber, whether natural such as India rubber and para rubber or synthetic such as polyisoprene, silicone rubber, polysulfide rubber and chlorinated and hydrochlorinated rubbers whether made from chlorine-containing monomers or by after-chlorination or hydrochlorination. Butyl rubber, as is known to those skilled in the art, is a copolymer of isobutene and a small amount usually under about 5 per cent, for example about 2 per cent, of a diene such as isoprene or butadiene, and may have molecular weights ranging from 10,000 to 2,000,000 or more. Butadiene rubber is the rubbery homopolymer of butadiene. Rubbery copolymers of butadiene with styrene, sold under the trade name GR-S, usually contain at least 50 percent butadiene, frequently about 75 percent butadiene, with the remainder being styrene. These rubbers are of course raw, i.e., in the uncured state.

The blend of this invention preferably contains from 60 percent to 98 percent by weight of polypropylene, and a total of from 2 percent to 40 percent of at least two rubbery materials, there being present at least 1 percent of each of two rubbery materials. Advantageously, the blend contains from 75 percent to 95 percent polypropylene and a total of from 5 percent to 25 percent rubber.

The compounding of the polypropylene with the rubbery materials can be done by malaxing, kneeding, milling or otherwise intimately blending them together in any convenient order in the desired proportions as by compounding the materials in an internal mixer such as a mixing extruder or a Banbury mixer or on an external mixer such as an open-faced roll mill to form intimately blended compositions.

Throughout the specification, parts and percentages are parts and percentages by weight unless otherwise specified. The examples which follow illustrate the invention but the invention is not limited thereto.

Example I

Eighty parts of polypropylene, 10 parts of butyl rubber, and 10 parts of polybutadiene are placed in a Banbury mixer. The polypropylene is an isotactic polymer having a molecular weight of 200,000 (calculated from a specific viscosity of 0.22 obtained from a solution of the polymer in decahydronaphthalene at a temperature of 135°C. and at a concentration of 0.1 gram of the polymer per 100 milliliters of solvent), a tensile yield stress of 340 kg/sq.cm., an elongation of 50 percent measured at a crosshead speed of 12.7 cm. per minute, a tensile modulus of 1.0 x 10 kg/sq.cm., a Rockwell 15X hardness of 165, a Vicat softening temperature of 152°C. and a melt index of 4.0 The butyl rubber is a copolymer of isobutylene with isoprene having an unsaturation of 0.8 mole percent and a Mooney viscosity of 50. The polybutadiene is a stereo-regular homopolymer of butadiene (94.5 percent cis-1,4; 5 percent trans-1,4) having a Mooney viscosity of 45.

The three materials are blended in the Banbury under a nitrogen atmosphere mixing first at low speed. The mixing speed is gradually increased until the temperature of the mixture reaches 190°C. The temperature is then held between 187°C. and 193°C. while the mixing is continued for six more minutes. The blend thus produced is cut into small chunks, cooled with dry ice and ground to fine granulation. The granules are formed by injection molding into test specimen bars and tested for impact resistance on an Izod type cantilever beam apparatus in accordance with ASTM D 256-56. Tests are run on both notched and unnotched specimens.

Unnotched specimens are tested at −17°C. and notched specimens are tested at −17°C. and 24°C. The −17°C tests conform to ASTM D 758-48. The unnotched specimens made from the blend of this example do not break. The notched specimens have an impact strength of 0.086 kg.meters/cm. at −17°C. and 0.24 kg.meters/cm. at 24°C.

Example II

There are placed in a Banbury mixer 80 parts of polypropylene, 10 parts of butyl rubber, both having the characteristics given for these materials in Example I, and 10 parts of GR-S. The GR-S is a copolymer of 77 percent butadiene and 23 percent styrene, having a Mooney viscosity number of 50. A 5 percent solution of the GR-S in styrene at 25°C. has a viscosity of 75 centipoises, and 5 percent solution of the GR-S in toluene at 25°C. has viscosity of 115 centipoises. These materials are blended, cut, granulated, molded and tested in a manner similar to that described in Example I. Unnotched test specimens of this polypropylene/dual rubber blend do not break at −17°C. Notched test specimens have an Izod Impact Strength of 0.06 kg.meters/cm. at −17°C. and 0.19 kg.meters /cm. at 24°C.

Examples III to XII

Blends are made, molded and tested in a manner similar to Examples I and II from polypropylene having the properties described in Examples I and II of butyl rubber, polybutadiene rubber or GR-S having the properties given in Examples I and II. The proportions of the materials in the blends are given in the Table below along with the test results. The symbols C_1, C_2, C_3 and C_4 denominate control compositions included in the Table for purposes of contrast.

TABLE

Example	Polypropylene (percent)	Butyl Rubber (percent)	Polybutadiene (percent)	GR—S (percent)	Impact Strength kg. meters/cm. −17° C.
III	80		10	10	.097
IV	82	9	9		.092
V	84	8	8		.08
VI	85	7.5		7.5	.04
VII	85		7.5	7.5	.06
VIII	86	7	7		.07
IX	88	6	6		.054
X	90	5	5		.05
XI	90	5		5	.038
XII	90		5	5	.05
C_1	80	20			.054
C_2	85	15			.02
C_3	90	10			.018
C_4	100				.018

The notched Izod impact strength test run at a temperature of −17°C. is a particularly sensitive test in that an improvement of as little as .01 kg.meter/cm. is regarded as significant.

As indicated above, any combination of at least two elastomers can be blended with polypropylene to produce the compositions of this invention provided there is present at least 1 percent of each of the two rubbers and the rubber content of the blend is preferably between 2 and 40 percent based on the combined weights of the rubber and the polypropylene. For example, a blend having characteristics similar to those of the examples can be made from 10 percent GR-S, 80 percent polypropylene, of the types used in the examples, and 10 percent natural rubber. A blend of polypropylene with three or more rubbers can be used to obtain the benefits of the invention, as for example, a blend of 85 percent polypropylene, 5 percent butyl rubber, 5 percent polybutadiene rubber and 5 percent of a rubbery copolymer of styrene and butadiene.

The quantities of the two or more elastomers used in the blend need not be the same. For example the blend can contain 1 percent butyl rubber and from 1 percent to 39 percent of one or more other elastomers, for example 20 percent of butadiene rubber. Another example of a composition according to this invention is 65 percent polypropylene, 5 percent butadiene rubber, 10 percent GR-S and 20 percent natural rubber.

All of the blends of this invention have improved impact strength over polypropylene alone. It has been found further, that the blends of this invention have improved impact strength at −17°C. than blends of polypropylene with a similar total amount of butyl rubber alone. With certain blends synergistic effects have been noted. For example, blends of polypropylene with butyl rubber and polybutadiene rubber have greater impact strength at −17°C. than do blends of polypropylene with similar total amounts of butyl rubber alone or polybutadiene rubber alone. Similarly blends of polypropylene with GR-S and polybutadiene have higher impact strengths at room temperature than do blends of polypropylene with similar total amounts of either of these rubbers blended one at a time.

The blends of the present invention can contain additives such as fillers, dyes, pig-

ments, antioxidants, stabilizers and the like and can be fabricated into useful articles by conventional fabricating techniques including molding, casting, calandering and extrusion.

WHAT WE CLAIM IS:—

1. A composition consisting of or containing a major proportion of isotactic polypropylene in intimate admixture with at least one percent by weight of each of at least two rubbery materials as specified herein.

2. Composition in accordance with Claim 1 characterized in that it contains from 60 to 98, preferably 75 to 95, percent by weight of polypropylene and 2 to 40, preferably 5 to 25, percent by weight of the two rubbery materials.

3. Composition in accordance with Claim 1 or characterized in that the rubbery materials are selected from butyl rubber, butadiene rubber, rubbery copolymers of butadiene with styrene, or polyisoprene.

4. Composition according to Claim 3 characterized in that it contains at least 1 percent of each butyl rubber and butadiene rubber.

5. Composition according to claim 4 characterized in that it contains 10 weight percent of butyl rubber and 10 weight percent cis - 1,4 - polybutadiene.

6. Composition according to Claim 3 characterized in that it contains at least 1 percent of each of butyl rubber and rubbery copolymers of butadiene with styrene.

7. Composition according to Claim 3 characterized in that it contains at least 1 percent of each of rubbery copolymers of butadiene with styrene and butadiene rubber.

8. Blends of a major proportion of isotactic polypropylene and at least one percent by weight of each of at least two rubbery materials as specified herein substantially as hereinbefore described.

9. Process for making polypropylene compositions of improved impact strength substantially as hereinbefore described with reference to the specific Examples I to XII.

10. Polypropylene compositions whenever prepared by the process claimed in claim 9.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.